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Characterization of Structure in Thin Polymer Resist Films

by

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Characterization of structure in thin polymer resist films

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ABSTRACT

We are investigating the structure and homogeneity of thin, multi-component resists prepared by spin casting and Langmuir Blodgett film formation technologies. Fluorescence spectroscopy has been used to evaluate various casting solvents for spin casting of multi-component films. Films of novolac containing pyrene as a small molecule probe were cast from various ethers and ether alcohols. The small molecules aggregated less when the dipole moment of the solvent closely matched that of the polymer. Langmuir-Blodgett techniques were used to create very thin (40 nm) films of novolac/diazoquinone. Images down to 1 μm were developed in these films and transferred into 50 nm of chrome. These very thin resist films could have various applications in advanced resist technologies, including mask making and deep UV lithography.

1. INTRODUCTION

Research on resist materials has centered primarily on the photochemistry of the sensitizer or photo-active compound (PAC). Although modifications to the PAC have been made to increase its sensitivity, improve its compatibility with the resin, or make it more sensitive deeper in the UV spectrum, in general the traditional novolac/diazoquinone positive photoresist has changed little over the years. The lithographic requirements placed on these materials, however, have changed drastically. UV lithography is presently being extended into the sub-micron regime. The smaller image dimensions require tolerances that are on the order of the dimensions of single polymer coils. Thinner resists are also desirable to achieve appropriate aspect ratios for these smaller images. All of these requirements stress the importance of having a homogeneous, well characterized resist film. It is clear that if we expect to maintain reproducible and dependable manufacturing processes in this regime, we must more fully understand the structure of these multi-component films, and be able to predict the effects of casting and processing parameters on the resist behavior. The present research program is directed toward improving the understanding of the structure of thin films on the molecular level, and the dependence of this structure on various casting and processing parameters.

Resist films are traditionally applied by spin casting. This casting method causes the film to dry while in a non-equilibrium state, with the resist materials kept under radial stress during the rapid solvent evaporation. The two components of most positive resists are not highly chemically compatible, so the casting solvent can have a large impact on the homogeneity of the cast film. Inhomogeneities in the resist film could cause variations in resist development rate and image dimensions. Previously, there have been no good methods to evaluate the homogeneity of resist films on the molecular level, or to compare the microscopic effects of various casting solvents. As a model system to study this, we have selected the aggregation of a dye in spin cast novolac films. We have replaced the standard diazoquinone sensitizer with pyrene, and have measured the aggregation of the pyrene using fluorescence spectroscopy. Pyrene was used as the small molecule dye due to its ability to form excimers. The formation of a pyrene excimer requires the two pyrene molecules to be in a co-planar sandwich structure with an inter-planar distance of about 4 Å. The excimer will only form upon excitation of one of the chromophores - the chromophores repel each other in the ground state. In solution, the chromophores can diffuse together during the rather long excited state lifetime (about 200 ns) of pyrene. In the solid state, however, the diffusion of molecules is severely limited, so the pyrene excimer can only be formed when pyrene molecules lie close enough together in the film to form an excimer upon excitation. In this way, the intensity of excimer and monomer emission after excitation is an indication of the local concentration of pyrene. This phenomenon has been used to monitor changes in small molecule aggregation in spin cast films.

There are many advantages to using thin resists for microlithography. It improves the aspect ratio for small image dimensions, and sidewall angle has a smaller impact on image dimensions. Moreover, if the resist can be made thin enough, the problems of novolac absorption in the deep UV can be minimized. Unfortunately, when

films are spun down to very small thicknesses, the problem of defects (pinholes) becomes unwieldy. It is very difficult to spin cast thin, continuous films. For this reason, we have also been investigating the use of Langmuir-Blodgett technologies to form resist films.¹

Langmuir films are formed by spreading a small quantity of an amphiphilic material onto the surface of a water subphase using a hydrophobic spreading solvent. The solvent evaporates leaving less than a monolayer of the desired material on the water surface. The surface area is then reduced, compressing the material to a compact monolayer. If a solid substrate is passed through this monolayer, the monolayer may be transferred onto the substrate, creating a Langmuir-Blodgett film. Thicker films can be built up by repeating this process and transferring many monolayers onto the substrate. Due to the deposition technique, LB films are highly ordered and allow the possibility of controlling the structure and composition of the final film. We have been investigating the potential of creating multilayer novolac/diazoquinone resist films on the order of 300-500 Å thick using LB techniques.

2. EXPERIMENTAL

2.1 Materials.

The casting solvents were obtained from Aldrich Chemical Company and were spectral grade except for the ethyleneglycol diethylether and the bis 2-ethoxyethyl ether. The solvents were used as received. The pyrene and pyrene butyric acid (PBA) were also obtained from Aldrich and were purified by recrystallization from toluene. The novolac sample was provided by Kodak, and was synthesized from pure meta-cresol and formaldehyde. It has a weight average molecular weight of 13,000 and a very broad polydispersity of 8.5. The polymer was purified by two precipitations from tetrahydrofuran (THF) into hexane. Pyrene tagged novolac was prepared by reacting pyrene butyric acid chloride with the phenolic group on the novolac,² resulting in the pyrene being covalently bonded to the polymer backbone through an ester linkage.

The LB films were formed from mixtures of novolac with a sensitizer provided by Fairmount Chemical Company. The sensitizer is a naphthoquinone-1,2-(diazide-2)-5-sulfonyl ester known under their trade name as positive sensitizer 1010. The spreading solvent was isopropyl acetate, which was obtained from Aldrich Chemicals and used as received.

2.2 Sample preparation of solvent cast films.

Films of pyrene-tagged novolac and solutions of pyrene and novolac were cast both by spinning and by static methods. The films were cast from solutions containing 20 wt% solids and various solvents including 2-methoxyethanol (MOE), 2-ethoxyethanol (EOE), 2-butoxyethanol (BOE), tetrahydrofuran (THF), ethyleneglycol dimethyl ether (EGDME), ethyleneglycol diethyl ether (EGDEE), 2-methoxyethyl ether (MOEE) and 2-ethoxyethyl ether (EOEE). The chromophore concentration was 0.2 mol ratio of pyrene to novolac monomer for both the tagged and untagged samples. The spin cast films were prepared by flooding a glass disc with the solution and spinning it at 4000 rpm for 90 sec. on a Metron System Inc. LS-8000 spinner. The films were approximately 1 µm thick. Some of the films were then placed under vacuum for up to 16 hr., but no changes in excimer ratio were observed. The static cast films were prepared by placing about 0.3 ml of solution on a glass disc, allowing it to air dry, and then drying the films under vacuum overnight.

2.3 Fluorescence instrumentation and measurements

Fluorescence spectra were measured on a Spex Fluorolog 212 spectrofluorometer with a 450 W xenon arc lamp and a Spex DM1B data station. Spectra were taken with front face illumination using a 343 or 348 nm excitation wavelength for the free or tagged pyrene, respectively. Monomer fluorescence was measured at 374 or 378 nm and excimer fluorescence was measured at 470 nm. Monomer and excimer peak heights were used to calculate the ratio of the intensity of the excimer to the intensity of the monomer, I_e/I_m .

2.4 Langmuir-Blodgett films and lithographic processing

The Langmuir-Blodgett films were fabricated using a Joyce-Loebl Trough IV. Various mixtures of novolac and diazoquinone were spread from isopropyl acetate onto a subphase of filtered deionized water. The pressure/area isotherms for the solutions were measured at 20°C and at a compression rate of 50 cm²/min. The films were

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compressed and expanded until two successive pressure/area curves were within about 2% of each other in the range of 5-10 dyn/cm. For solutions with more than 10% PAC, this occurred for the first and second compressions. The solutions with 10% PAC or less required three compressions. The collapse pressure of the PAC was defined as the point where a negative deviation in the slope of the pressure/area isotherm occurred. There is no observable collapse pressure for novolac by this definition, although a gradual decrease in surface area with time will occur at higher pressures (>10 dyn/cm).

The films were transferred onto Si wafers having a 50 nm Cr coating at surface pressures of 2.5 - 10 dyn/cm and a substrate dipping rate of 2 mm/min. The films were composed of 15 - 20 monolayers, with an average film thickness of about 40 nm as measured by ellipsometric methods. The films were exposed on a Canon FP-141 (primarily g-line) at an exposure setting of 5.0 using a standard fine line test pattern that contains line/space pairs down to 1 μ m (2 μ m pitch). The wafers were developed in 0.1-0.2 M KOH, depending on the PAC content. The wafers received a 20 min. 120 C post development bake to improve adhesion to the chromium. The chrome was etched in Cyantek CR-14 chromium etchant.

3. RESULTS AND DISCUSSION

3.1 Solvent cast films

The homogeneity of cast films can be very dependent on the casting conditions, including the casting method and solvent. If films are allowed to form very slowly, as is the case for static cast films, the slow solvent evaporation allows more time for the components of the film to reach thermodynamic equilibrium. If the components are not highly compatible, they may phase separate during casting. Spin casting causes the solvent to evaporate very rapidly, even for fairly high boiling solvents. This may not allow sufficient time for extensive rearrangement of the components of the film during the casting process. Therefore, the homogeneity may be influenced by the interactions of the components with the solvent, and the solvents ability to moderate the incompatibility of the materials. In previous work,³ we observed that the level of excimer fluorescence (and, hence, the level of aggregation) varied for films cast from diglyme (MOEE) and cellosolve (EOE), while I_e/I_m for films cast from THF was similar to that obtained from diglyme. In general, however, the solvent properties of cellosolve and diglyme are much more similar than those of THF. In the present work, we have studied a broader range of solvents to evaluate the effect of various solvent parameters (viscosity, boiling point, hydrogen bonding, polarity, and evaporation rate) on film casting. Many of the solvents are similar to casting solvents presently in use for photoresists.

Table 1. I_e/I_m for Solvent Cast Films

Solvent	Spin Cast Free Pyrene	Spin Cast Tagged Pyrene	Static Cast Tagged Pyrene
EOE	8.19	2.96	3.02
BOE	7.53	2.53	2.72
THF	4.38	2.46	2.24
EGDME	4.36	2.76	2.92
EGDEE	6.05	2.64	2.92
MOEE	4.78	2.05	1.97
EOEE	5.31	2.17	2.53

Significant variations in pyrene aggregation were observed for films cast by spin and static casting methods. The chemical incompatibility of the novolac and pyrene was verified by the observation of pyrene crystallites in all of the static cast films that contained free pyrene. Fluorescence spectra were not taken of these films. The spin cast films made from these same solutions did not exhibit visible pyrene crystallites, probably due to the speed of film formation. In every case, though, the spin cast films with free pyrene had a higher I_e/I_m than the equivalent films cast from pyrene-tagged novolac; in most cases I_e/I_m for the films with free pyrene was at least twice that for the tagged pyrene (Table 1). The pyrene that was tagged onto the novolac backbone has fairly limited mobility; therefore, it can be used as a control for the case of well dispersed pyrene. By comparison, the free

pyrene was obviously not well dispersed, but had aggregated even during the rapid process of spin casting. The pyrene concentration of 0.2 mol% equates to about 30 weight%, which is still within the range of common sensitizer loading for resists. It is therefore probable that low levels of PAC aggregation also occur during the casting of resist films.

The static cast films of tagged pyrene had slightly higher I_e/I_m than the equivalent spin cast films (Table 1), indicating the thermodynamic preference of the two components to separate is largely damped by the constraints placed on the mobility of the pyrene due to tagging. The static cast pyrene-tagged films still had much lower I_e/I_m values than the spin cast films with free pyrene. The attachment of the pyrene to the polymer chain limits its ability to aggregate much more than does the rapid solvent evaporation during spinning.

As can be seen from Table 1, variations in I_e/I_m were observed for the different casting solvents. Of the various solvent parameters evaluated, we found that I_e/I_m was most closely correlated to the dipole moment of the casting solvent. In all three cases - spin cast/free pyrene, spin cast/tagged pyrene, and static cast/ tagged pyrene - there was a minimum in I_e/I_m at a dipole moment of about 1.8 - 1.9 D (Figure 1). This correlates fairly well with the reported value of about 2.0 D for phenolic novolac⁴ rather than with the pyrene, which has a dipole moment of 0 D. The optimum film homogeneity was achieved by matching the dipole moment of the casting solvent to that of the matrix polymer rather than to the dye molecule. This could be a useful criterion when choosing a casting solvent for photoresists.

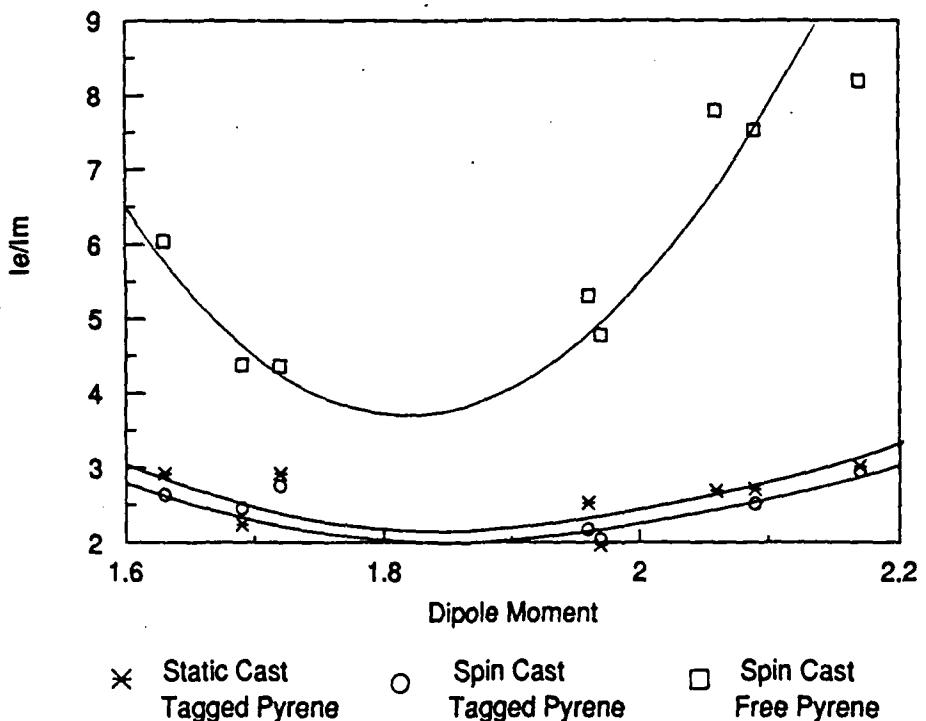


Figure 1. I_e/I_m vs solvent dipole moment

3.2 Langmuir-Blodgett films

We have succeeded in making LB films of novolac, diazoquinone, and mixtures of the two that were from 5 to 50 weight percent diazoquinone. Novolac monolayers are significantly thicker than those of other linear polymers. A single layer of novolac is about 2.5 nm thick as opposed about 1.0 nm for a monolayer of PMMA.¹ This may result because the novolac is a branched polymer that may not lie entirely flat on the water surface. The novolac films also exhibited much greater thickness variations than other linear polymers such as PMMA and poly(p-hydroxystyrene). We are still investigating the source of these variations.

While we have not yet used fluorescence techniques to observe aggregation in LB films of the novolac/PAC mixtures, pressure/area measurements and collapse pressures are conventionally used as a measure of the solubility of two component films.⁵ PAC has a very obvious collapse pressure at about 24 dyn/cm after which the curve "plateaus" such that decreases in surface area will not cause any increase in the pressure on the film. There is no such obvious change in the slope of the pressure/area curve for novolac. When Langmuir films of novolac and PAC mixtures are compressed, the "plateau" (which we consider to be the collapse of the PAC) is still observable for mixtures with at least 50% PAC, though the width of the plateau decreases and the pressure at which it occurs increases with decreasing PAC concentration (Figure 2). If the two components were segregated into distinct phases, the collapse pressure should remain constant.⁶ Hence, it appears that we have a solution of the two components on the water surface.

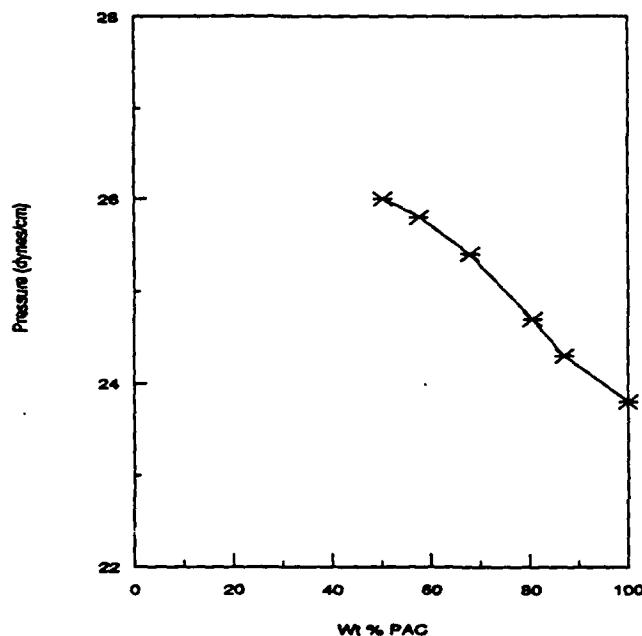


Figure 2. Collapse pressure vs composition.

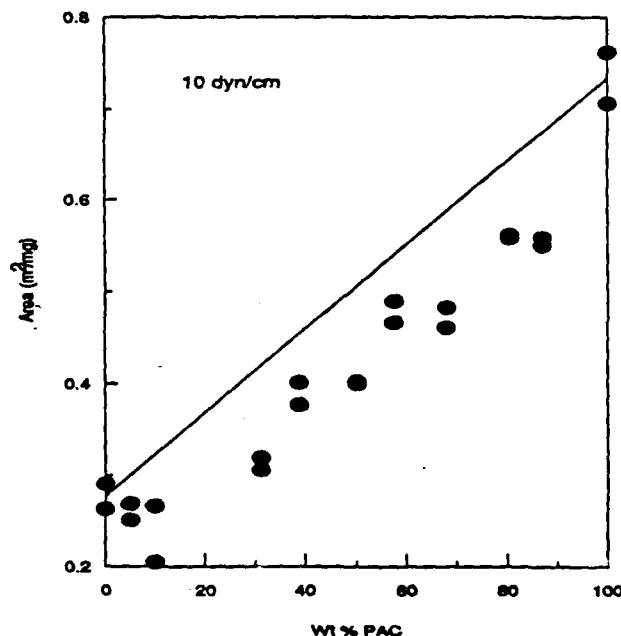


Figure 3. Surface area vs composition.

Another method for determining the homogeneity of the Langmuir film is to measure the surface area required by the mixtures at a given pressure. If the compounds form an ideal solution, the surface areas of the mixtures should lie on the line connecting the surface areas of the two pure compounds (Figure 3). Deviation from this behavior indicates that the materials are forming a non-ideal solution. In the case of novolac and PAC, there is a slight negative deviation from ideality. The mixed films have a slightly smaller surface area than would be predicted for an ideal solution, indicating that a stabilizing interaction exists between the materials. It is possible that the small molecule is able to fill some of the free volume associated with the polymer coils. The deviation of the area is fairly small, indicating that the films are fairly homogeneous.

Images were obtained in the films from PAC/novolac mixtures from 5 to 50 weight% PAC, although the films composed of 50% PAC developed very slowly, and may not have cleared completely. The images were successfully transferred into the chrome substrate for the films containing 10, 20, and 30% PAC. The 1x1 μm arrays in resist and in chrome for the 10% films are shown in Figures 4 and 5. The images from the 5% film did not stand up as well to the etchant, as can be seen in Figure 6. The images from the 40 and 50% films did not transfer well into the chrome indicating that some of the organic materials remained in the developed regions even after developing.

We have succeeded in making and transferring small images from very thin LB films. While we have not yet performed a controlled pinhole study, few have been observed in the films that contain at least 10% PAC. We have, however observed defects of a different nature. Many of the films exhibited streaks that do not develop out, even in the exposed regions. These may be due to small areas that are higher in PAC concentration which

are not obvious from the overall pressure/area relationships. We will continue to study the structure of these mixed Langmuir films and the composition and homogeneity of the final LB films.

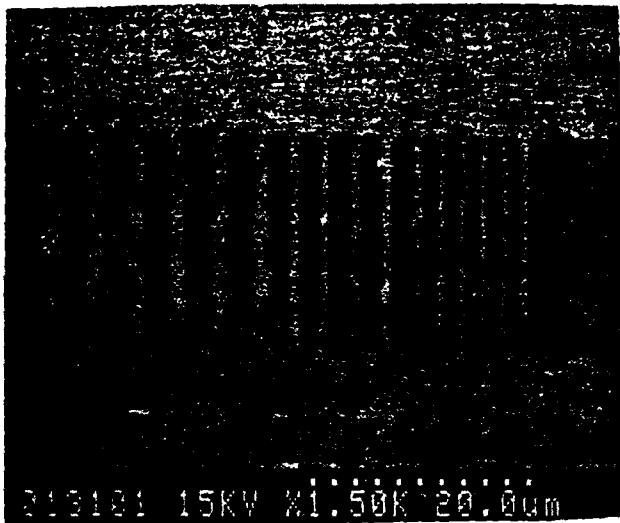


Figure 4. Resist images in LB films with 10% PAC. The smallest images are 1x1 μm arrays.

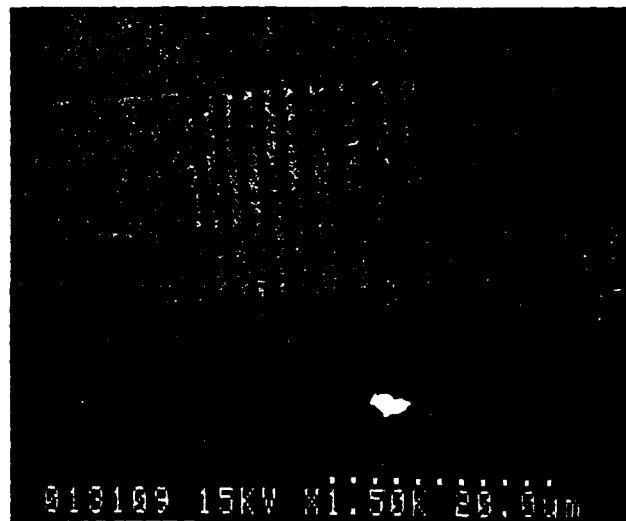


Figure 5. Images etched into 50 nm chrome from 10% PAC resist.

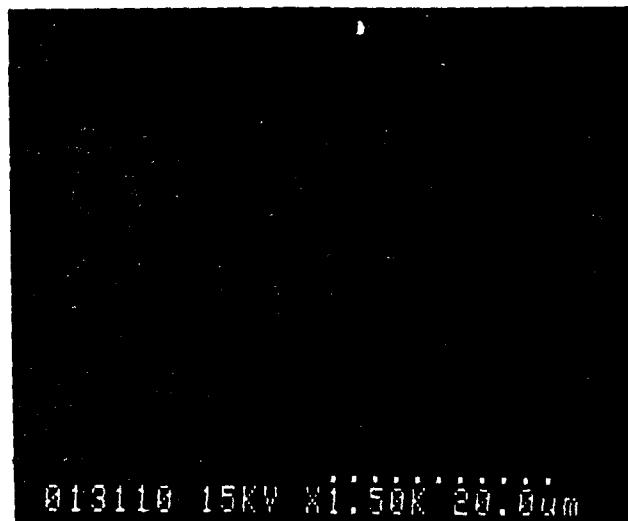


Figure 6. Images etched into 50 nm chrome from LB films with 5% PAC.

4. CONCLUSIONS

The homogeneity of a solvent cast two component film can be affected by many factors, including the component interactions, the method of casting and the choice of casting solvent. For most resists, the components and casting technique are essentially predetermined, and difficult to change. The choice of casting solvent should be more open, however. This research has indicated that the choice of casting solvent can strongly affect the extent of aggregation of dyes in multi-component spin cast films, and that the casting solvent should be chosen so that the dipole moment of the solvent matches that of the polymer.

We have also shown that Langmuir-Blodgett technologies may be viable to create thin, continuous films of standard positive resist materials. Images have been developed and transferred into 500 Å chrome from as little as 400 Å of resist. Films in this thickness range would allow very high resolution and allow use of conventional resist materials down into the deep UV.

5. ACKNOWLEDGMENTS

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